LETTER

High-pressure synthesis of Na$_2$Mg$_6$Si$_6$O$_{18}$(OH)$_2$—a new hydrous silicate phase isostructural with aenigmatite

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Abstract

A new hydrous phase, Na$_2$Mg$_6$Si$_6$O$_{18}$(OH)$_2$, which is isostructural with aenigmatite, was synthesized at 10 GPa and 1250 °C and its structure studied with X-ray diffraction data collected from a twinned crystal on a CCD diffractometer. The unit-cell parameters are $a = 10.2925(9)$, $b = 10.7052(9)$, $c = 8.8027(10)$ Å, $\alpha = 105.280(2)$, $\beta = 96.712(2)$, $\gamma = 125.256(2)^\circ$, and $V = 718.1(5)$ Å$^3$. The structure refinement indicates that O4 and O14, the only 2 O atoms that are not bonded to Si, are protonated. The presence of OH in the structure is confirmed by an unpolared Raman spectrum. Compared to anhydrous sodic phases with the aenigmatite-type structure, silicate chains in hydrous Na$_2$Mg$_6$Si$_6$O$_{18}$(OH)$_2$ are more kinked, resulting in relatively long average Na-O distances.

Introduction

Aenigmatite-group minerals, albeit minor, are relatively common constituents of a variety of volcanic, plutonic, metamorphic, and metasomatic rocks; they also occur in meteorites (e.g., Deer et al. 1997). The composition of aenigmatite-group minerals conforms to a general formula A$_2$B$_6$T$_6$O$_{20}$, where A cations are sevenfold or eightfold-coordinated Na and Ca, B octahedrally coordinated Fe$^{2+}$, Fe$^{3+}$, Mg, Al, Cr, Ti, and Sb$^{5+}$, and T tetrahedrally coordinated Si, Al, Mg, Al, B, and Be. There are two crystallographically distinct A sites (M8 and M9), seven B sites (M1-M7), and six T sites (T1-T6) in the aenigmatite-type structure. Eight graphically distinct A sites (M8 and M9), seven B sites (M1-M7), whereas the B-, Be-, Sb-, and/or Cr-bearing members (welshite, høgtuvaite, serendibite, and krinovite) are rare. Kunzman (1999) thoroughly reviewed the minerals of the aenigmatite-rhönite group. In addition, several high-temperature synthetic phases have been reported to possess the aenigmatite-type structure, silicate chains in hydrous Na$_2$Mg$_6$Si$_6$O$_{18}$(OH)$_2$ being isometric with aenigmatite. This result suggests that the stability of aenigmatite-group minerals could be much greater than was evident so far and phases with the aenigmatite-type structure could play a more important role in the deeper mantle than in the Earth’s crust. Here we report results of the single-crystal structure analysis of a hydrous silicate phase, Na$_2$Mg$_6$Si$_6$O$_{18}$(OH)$_2$, synthesized at high pressure, which represents the first aenigmatite-type structure containing OH.

Experimental procedures

The Na$_2$Mg$_6$Si$_6$O$_{18}$(OH)$_2$ sample was synthesized in a multi-anvil apparatus at 10.0 GPa and 1250 °C for 10 hours. The starting composition in weight percent of SiO$_2$ (46.1), Al$_2$O$_3$ (2.6), MgO (28.9), Na$_2$O (20.9), and H$_2$O (1.5) was designed to study high pressure breakdown products of amphibole. The starting material was prepared from high purity (99.999%+) SiO$_2$, Al$_2$O$_3$, MgO, and Na$_2$CO$_3$, with water added to the anhydrous and decarbonated oxide mix as brucite. After the run, the Pt$_{100}$ sample container was embedded in epoxy resin and ground to expose the center of the charge, in which two different phases were found: hydrous Na$_2$Mg$_6$Si$_6$O$_{18}$(OH)$_2$ forming isometric crystals up to ~80 μm in diameter concentrated at the cooler end of the capsule and anhydrous Na$_2$Mg$_2$Si$_2$O$_7$ forming large blocky crystals up to ~300 μm in the largest dimension. The phase composition was determined with an electron microprobe (JEOL superprobe) using analytical conditions of 15 kV and 5 nA with a rastered beam size of 20 μm to minimize electron beam damage. Pure SiO$_2$, MgO, Al$_2$O$_3$, and synthetic omphacite were used as standards with 20 s on peaks and 10 s on backgrounds of the X-ray lines. The average composition of Na$_2$Mg$_6$Si$_6$O$_{18}$(OH)$_2$ from 12 measurements was found to be in wt% SiO$_2$: 52.5(3), Al$_2$O$_3$: 3.6(2), MgO: 31.6(3), and Na$_2$O: 9.2(2) with a total oxide sum of 96.6(6) wt%. Given the results of the structural analysis, the chemical formula was calculated on the basis of 18 O atoms + 2 OH, resulting in Na$_2$Mg$_5$Si$_5$O$_{18}$(OH)$_2$ with a stoichiometric H$_2$O content of 2.6 wt%.

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